Coherent control of lattice deformations in quantum wires by optical self-trapping

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We investigate theoretically a semiconductor quantum wire under the effect of an intense off-resonant cw laser. We show that in the regime of strong exciton-phonon coupling the light-dressed ground state of the wire reveals symmetry-breaking features, leading to local lattice deformations. Due to the off-resonant nature of the excitation, the deformations are reversible and controllable by the intensity and frequency of the laser. We calculate the light-induced strain forces on the lattice in the case of an organic quantum wire.

When an atomic system or a semiconductor is irradiated by a pump laser in the transparency spectral region, it responds to the field with its dynamic polarizability and gains a polarization energy.[1] In the case of semiconductors, this dynamic Stark effect is well understood in terms of the creation of virtual electron-hole pairs (excitons) across the band gap by pump photons,[2] and it explains the excitonic blue shift experimentally observed.[3] It has been recently pointed out that the dynamic polarization can be used as a quantum control tool in semiconductors. For instace, the virtual excitons created by an off-resonant pump field interact with spins localized by impurities or quantum dots and can create a local magnetic field,[4] induce spin-spin coupling,[5,6] and paramagnetic to ferromagnetic transitions.[7]

In this paper we will show that the dynamic optical polarization can be used to induce strain forces and control lattice deformations in a semiconductor quantum wire. If the virtual excitons created by the pump field interact strongly with phonons in the lattice, a self-trapping[8] of the optical polarization results. This induces local forces on the lattice. As in the case of the optical spin control, there is no absorption of energy since the pump photons are tuned in the transparency region: the effect is due to radiative (stimulated) corrections to the ground state of the system. The coherent nature of the effect makes it reversible and finely controllable with lasers. In principle many different materials have the exciton-phonon coupling strong enough for this optical self-trapping effect.[9] Here we focus on an organic one dimensional system, polydiacetylene (PDA),[10] which has been studied for its strong nonresonant optical nonlinearities and exciton-phonon effects. Phonon-mediated optical nonlinearities have been observed in this material.[11]

Recently-developed experimental techniques can detect light-induced lattice displacement in molecules and semiconductor systems. Examples include pump-probe electron diffraction[12] and ultrafast x-ray absorption spectroscopy.[13] These techniques can be extremely sensitive and measure laser-induced lattice dynamics within picosecond and milli-Ångström resolution.[14] PDA has been already identified as a good system where the vibrational dynamics after optical excitation could be observed,[15] and the possibility of addressing optically a single polymer chain of this material has been recently demonstrated.[16] We are focusing here on the steady state regime of the polymer driven by a cw or nanosecond laser. This should be easier to address experimentally, yet it contains rich and unexplored features related to light-matter interaction in strong coupling. We remark that, in contrast to more common schemes based on photothermal effects, the coherence of the electronic excitation is a key element in this light-induced effect.[17]

The coherent many-body ground state of the wire in the presence of the light field can be parametrized as a BCS-like wavefunction that depends on variational parameters. By a functional minimization of the ground state energy with respect to these variational parameters, we obtain a non-homogeneous nonlinear equation that describes the distribution of the optical polarization in the wire. Unlike the case of a single exciton-polaron,[18] the total polarization is not fixed but is determined by the intensity and frequency of the laser field. The nonlinear equation is solved numerically to calculate the distribution of the polarization and therefore the strain forces acting on the wire. Recent esperiments on single PDA chains[16,19,20] suggest that free excitonic states have a Bohr radius of 1-2 nm, corresponding to 2-4 monomer molecules, and a mass of $0.3m_0$. We use these parameters to describe the wire with a tight-binding model. The model takes explicitly into account the exciton-light coupling. The hamiltonian can be written as

$$H = H_{SSH} + H_{XL} \ , \tag{1}$$

where the first term has a Su-Schrieffer-Heeger (SSH)[21] form

$$\begin{aligned} H_{SSH} \ &= \ \sum_n \frac{p_n^2}{2M} + \sum_n \frac{C}{2}(u_{n+1}-u_n)^2 \\ &\quad - \sum_n t_{n+1,n}(B_{n+1}^\dagger B_n + B_n^\dagger B_{n+1}) \ , \end{aligned} \tag{2}$$

and the exciton-light interaction is described by

$$H_{XL} = \sum_n \frac{\Omega}{2}(B_n^\dagger + B_n) + \sum_n (E_g + 2t_0 - \hbar\omega_L) B_n^\dagger B_n \ . \tag{3}$$

M, C, u_n and p_n are the mass, elastic constant, total displacement and momentum of the n-th site of the tight-binding chain. B_n^+, B_n are operators of creation, annihilation of excitons in a singlet spin state. The hopping term is $t_{n+1,n} = t_0 - \gamma(u_{n+1} - u_n)$, where γ is related exciton-phonon deformation potential interaction:

$D = 2\gamma a$. a is the site separation in the tight-binding chain taken equal to the excitonic Bohr radius (1.5 nm for PDA). The value of t_0 is determined by the exciton effective mass m as $t_0 = \hbar^2/2ma^2$. We treat the exciton-light coupling (H_{XL}) semiclassically, and the rotating wave approximation is assumed. The shift $2t_0$ is introduced in such a way to define E_g as the $k = 0$ exciton energy at the bottom of the band, and ω_L is the frequency of the laser. $\Omega = d\mathcal{E}_0$ is the Rabi energy due to the dipolar coupling of excitons with a light field of amplitude $\mathcal{E}_0$. We remark that PDA has a large exciton binding energy (of the order of 500 meV) and also shows vibronic resonances spectrally localized at about 200 meV below the free exciton peak.[20] If the optical detuning $\delta = E_g - \hbar\omega_L$ is small compared to these quantities, both free e-h pairs and vibronic excitations can be neglected in the model.

In contrast to the polyacetylene case,[21] the ground state of polydiacetylene is a non-degenerate state that we can express in the form

$$|\Phi_0\rangle = \prod_n |0\rangle_n \tag{4}$$

meaning that the wire has no excitons. However, in the presence of light, the coherent light-dressed ground state will change, and we write it using the ansatz[22]

$$|\Phi_\Omega\rangle = \prod_n \left(\alpha_n|0\rangle_n + \beta_n e^{i\varphi_n}|1\rangle_n\right) \ , \tag{5}$$

where α_n, β_n, and φ_n are variational parameters, and α_n and β_n are subject to the single-occupancy constraint $|\alpha_n|^2 + |\beta_n|^2 = 1$. $|0\rangle_n$ and $|1\rangle_n$ denote the number of excitons in the site n. Due to the hopping, the variational coefficients depend on the index n. We introduce the phases φ_n to make α_n and β_n real. The mimimum of the total energy occurs when the phases are constant, making all the two-level oscillators in the chain mutually coherent.[23] Using the wavefunction in Eq.(5) and the full Hamiltonian in Eq. (1), we calculate the total energy. By introducing the optical polarization function

$$\psi_n = -\langle B_n\rangle = 2\alpha_n\beta_n \ , \tag{6}$$

the energy can be written as

$$-\frac{1}{2}\left(\sum_n t_{n+1,n}\psi_{n+1}\psi_n + \Omega\sum_n \psi_n + \delta'\sum_n \sqrt{1-\psi_n^2}\right), \tag{7}$$

(terms that do not depend on ψ_n have been dropped) where we have defined $\delta' = \delta + 2t_0$. We also have set $\varphi_n = \pi$, and assumed $\alpha_n\beta_n > 0$ and $|\alpha_n| > |\beta_n|$. By functional derivation with respect to ψ_n we obtain

$$-t_{n+1,n}\psi_{n+1} - t_{n,n-1}\psi_{n-1} - \Omega + \delta'\frac{\psi_n}{\sqrt{1-\psi_n^2}} = 0 \ , \tag{8}$$

which in the continuum limit reads

$$-t_0\left(2\psi_n + \frac{\partial^2\psi_n}{\partial n^2}\right) + 2\gamma\psi_n\frac{\partial u_n}{\partial n} - \Omega + \delta'\frac{\psi_n}{\sqrt{1-\psi_n^2}} = 0. \tag{9}$$

In order to have a closed equation for ψ_n we need to find $\partial u_n/\partial n$, which depends self-consistently on the distribution of the polarization along the chain in the steady state. This can be calculated using the same approch of Ref. 18 by writing the classical equations of motions for the wire

$$M\ddot{u}_n = -\frac{\partial\langle H\rangle}{\partial u_n} = C(u_{n+1} - u_n) - C(u_n - u_{n-1}) + F_n \ . \tag{10}$$

In the continuum limit the strain force on the site n, F_n, is related to the gradient of the polarization density as

$$F_n = \frac{\gamma}{2}\frac{\partial|\psi_n|^2}{\partial n} \ . \tag{11}$$

Since we are considering a stationary solution in the presence of the light we set Eq. (10) to zero, which gives the local displacement due to the strain force as $u_n = -C^{-1}\int\int F_n\, d^2n$. Then from Eq. (11) we find

$$\frac{\partial u_n}{\partial n} = -\frac{\gamma}{2C}|\psi_n|^2 + a\Delta \tag{12}$$

where Δ is a dimensionless constant of integration that gives finite-size effects. We choose $\Delta = 0$, which implies that the total lenght of the wire is not fixed. This choice does not affect the results in the limit of a wire much longer than the extension of the self-trapping region. The force constant C can be expressed in terms of the sound velocity S as $C = S^2M/a^2$ where $S = 2.5\times10^3$ m s^{-1} for PDA.[19] Finally, from Eqs. (9) and (12) we get the equation for ψ_n

$$2t_0\left(\frac{1}{\sqrt{1-\psi_n^2}} - 1\right)\psi_n - t_0\frac{\partial^2\psi_n}{\partial n^2} - \frac{D^2}{4MS^2}\psi_n^3 - \Omega + \delta\frac{\psi_n}{\sqrt{1-\psi_n^2}} = 0. \tag{13}$$

Notice that we are dealing with a system where the quantity ψ_n is not normalized. The amount of total polarization density in the wire, i.e. the number of virtual excitons, is determined by the external field parameters Ω

and δ. The first term in Eq. (13) describes the blue shift of the exciton (Pauli blocking). The cubic term, related to the exciton-phonon deformation potential interaction D, is responsible for the self-trapping of the polarization. It corresponds to an attractive potential proportional to the polarization density. The last term takes into account the effect of the finite optical detuning of the laser field. In the absence of light (i.e. for $\Omega = 0$), the solution to Eq. (13) is $\psi_n = 0$ corresponding to the trivial solution in Eq. (4). In the absence of hopping between the sites ($t_0 = 0$, $D = 0$), we have spatially separated excitations with no constraints applied.[22] The solution in this case corresponds to the one of the dynamic Stark effect in atoms[1]

$$\psi_n = \frac{\Omega}{\sqrt{\delta^2 + \Omega^2}}. \tag{14}$$

At resonance ($\delta = 0$) Eq. (14) gives the maximum occupation $\psi_n = 1$, corresponding to half exciton per site, and the light-dressed ground state is $2^{-1/2}(|0\rangle - |1\rangle)$ on each site. In the limit of small excitation $\psi_n \ll 1$, Eq. (13) is similar to a one-dimensional nonlinear Schrödinger equation with a cubic attractive nonlinearity. It is known that a Bose-Einstein Condensate (BEC) with an attractive nonlinearity breakes symmetry in 1D so that the ground state does not correspond to a constant amplitude solution.[24] In our case, these real symmetry-breaking solutions for the ground state describe the optical self-trapping effect. In the small excitation limit some analytical forms for the solution of Eq. (13) can be written in terms of Elliptic functions using Cayley's transformations.[23] It is interesting to remark that the Hamiltonian in Eq. (1) can be mapped to an XY model for spins coupled to phonons. The Rabi energy describes an external magnetic field in the XY plane while the optical detuning corresponds to a magnetic field in the Z direction. An effective nonlinear interaction between spins analogous to our cubic term was found in the case of a classical Heisenberg spin chain coupled to phonons.[25]

In order to study on the same ground the inter-cell hopping and the presence of electromagnetic field we solve numerically Eq. (13). This allow us to calculate the forces on the lattice for an arbitrary value of the external field, provided the system remains coherent. To solve the equation numerically, we use the steepest descent method of functional minimization.[26] This method is efficient in solving numerically Gross-Pitaevskii equations for BECs, which are in the same class of Eq. (13).[27] We start from an initial trial function $\psi_n(0)$, then $\psi_n(\tau)$ is evaluated in terms of the equation $\frac{\partial \psi_n(\tau)}{\partial \tau} = -\mathcal{H}\psi_n(\tau)$, by choosing an arbitrary step $\triangle\tau$ in the fictitious time variable τ and by iterating according to $\psi_n(\tau + \triangle\tau) \approx \psi_n(\tau) - \triangle\tau\mathcal{H}\psi_n(\tau)$. The nonlinear operator $\mathcal{H}$ is defined in such a way that $\mathcal{H}\psi_n(\tau) = 0$ corresponds to Eq. (13). At convergence, the condition $\frac{\partial \psi_n}{\partial \tau} = 0$ gives the solution to Eq. (13).

The results of the numerical solution for ψ_n are shown in Fig. 1. The linear density of the wire is 1.4×10^{-14} g/cm.[18]. The sum of the deformation potentials for the conduction and valence band is $D = D_c + D_v = 6.1$ eV.[19] The dipole momentum of PDA is 10.1 eÅ,[28] and the energy of the excitonic (singlet) state is 2.282 eV.[16] The numerical solution is obtained in a chain with 100 sites and periodic boundary conditions are used. The total lenght of the chain is smaller than the wavelength of the light and we can neglect the effect of a finite photon wavevector. The experimental value of the excitonic linewidth at 10 K is 350 μeV,[16] which is much smaller than the values for the Rabi energy and detuning we use in the calculations. We have also checked that the exciton-polaron binding energy is always smaller than δ. Fig. 1 shows $|\psi_n|^2$ for three different values of the Rabi energy and the same optical detuning $\delta/t_0 = 0.05$ ($t_0 = 70$ meV) as a function of the site number. We estimate that the value of the Rabi energy needed for self-trapping corresponds to laser intensities of about 2.5 kW/cm^2, which is reasonable for nanosecond pulses. At the lowest value of the Rabi energy the polarization is small and homogeneously distributed along the wire. For $\Omega \sim 150\mu eV$, the solution is localized due to the phonon-assisted self-trapping. When the Rabi energy increases slightly, the polariza-

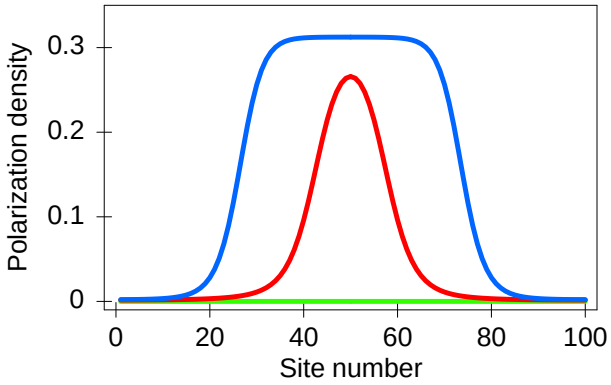

FIG. 1: (Color online) Polarization density $|\psi_n|^2$ for $\delta/t_0 = 0.05$, $\Omega/t_0 = 10^{-4}$ (green line), $\Omega/t_0 = 1.99 \times 10^{-3}$ (red line), and $\Omega/t_0 = 2.06 \times 10^{-3}$ (blue line)

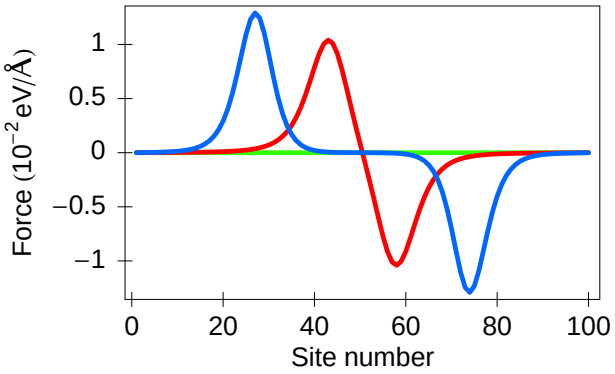

FIG. 2: (Color online) Force as a function of the site number for $\delta/t_0 = 0.05$, $\Omega/t_0 = 10^{-4}$ (green line), $\Omega/t_0 = 1.99 \times 10^{-3}$ (red line), and $\Omega/t_0 = 2.06 \times 10^{-3}$ (blue line)

tion distribution becomes broader and flatter at the top. This saturation is related to the intrinsic fermionic nature of the excitons. Notice that the total polarization increases when the Rabi energy increases. A gradient in the density of polarization produces a force on the ions according to Eq. (11). The force is stronger at edges of the $|\psi_n|^2$ distribution as seen in Fig. 2, and is positive to the right from the center of the chain and negative to the left. The quantity that is measured in electron or x-ray diffraction experiments would be $\partial u_n/\partial n$, i.e. the local deformation due to the light-induced changes in the lattice. For the parameters considered above, this quantity is in the range 10-100 mÅ, which is reasonable for an experimental observation of the effect.

We have neglected exciton-exciton Coulomb effects which may affect the picture given here, especially in the high excitation regime. This deserves further investigations. However, it is known that the BCS variational ansatz in Eq. (5) provides a good description of the ground state of an electron-hole system both in the low excitation regime (excitonic BEC) and in the high excitation regime (BCS pairing).[29] The fact that the electron-hole system here is driven by an external coherent field (laser) gives an additional justification to this ansatz since light-dressing can reduce Coulomb features beyond mean field like screening and broadening.[30] Finally, exciton-exciton interaction in the dynamic Stark shift can be neglected when the optical detuning is bigger than the biexciton binding energy,[2] therefore its effect can always be reduced by increasing the optical detuning.

In conclusion, we have investigated the effect of an intense off-resonant laser field in polydiacetylene chains. We have extended the SSH model to include the effect of a control laser field semiclassically. We have obtained a nonlinear inhomogeneous equation describing the spatial distribution of the optical polarization in the chain in the steady state. We find solutions describing self-trapping of the polarization which saturate when the intensity of the field is increased. The results suggest that local steady state lattice deformations can be finely controlled by the intensity and frequency of an intense laser field. This control scheme could have interesting applications to other organic materials where a strong exciton-phonon interaction exists, like e.g. in J-aggregates, or DNA.[31]

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